Continuum Models for Multiphase EOS

Carl W. Greeff, T-1

Shock wave and other dynamic compression experiments can reveal a wealth of information about phase transitions, which are often manifested as anomalies in the wave shape [1]. Detailed analysis of time resolved data, as obtained for instance by laser velocity interferometry (VISAR), can give information about transition kinetics on time scales from a few to hundreds of nanoseconds. Because of the complexity of wave propagation in phase transforming media, numerical simulation is an important tool for interpreting such experiments. An important component of such simulations is to model phase transition kinetics in a way that is computationally tractable, and accurately represents the phenomenon.

The standard treatment for dynamic phase transitions in such simulations is to regard each macroscopic region of the sample as containing fractions $\{\lambda\}$ of the various possible phases, with pressure and temperature equilibrium among the coexisting phases. Thermodynamic properties of the individual phases are described by their Helmholtz free energies $F_i(V_i,T)$ [2, 3]. Supplementing the free energies with a kinetic rule for evolving the λ_i in time fully specifies the hydrodynamic equation of state (EOS).

Following the pioneering work of Hayes [4] on transitions in bismuth, a widely used model is

$$\dot{\lambda}_i = \sum_j \alpha_{ij}\left(G_j - G_i\right) \qquad (1)$$

where G is the Gibbs free energy, and the α_{ij} are positive phenomenological rate coefficients. Equation (1) allows for finite transformation rates relaxing toward equilibrium. In spite of its apparent simplicity, Eq. (1) is awkward to apply in practice, because the constraints

$$\sum_i \lambda_i = 1$$

and $0 \le \lambda \le 1$ must be imposed externally. At fixed pressure and temperature, Eq. (1) leads to linear variation of λ_i with time, which is in qualitative disagreement with experimental data.

In considering the origins of these difficulties, it becomes clear that it is natural to describe the rate of transitions from phase i in relation to the amount of material in that phase. The result is that, in place of Eq. (1), one is led to the master equation,

$$\dot{\lambda}_i = \sum_j \lambda_j R_{ji} - \lambda_i R_{ij} \qquad (2)$$

where the rate coefficients R_{ij} are non-negative and describe the fractional transformation rate from phase i to phase j. Equation (2) has the practical advantage that the normalization constraint is naturally preserved. The fractions λ_i asymptotically approach 0 or 1, but never exceed these bounds. The asymptotic approach to complete transformation is in qualitative agreement with experiments [5].

It remains to describe the dependence of the R_{ij} on the thermodynamic state. In contrast to the linear dependence on the Gibbs free energy difference described by Eq. (1), our work on the $\alpha-\omega$ transition in Ti and Zr [6] indicates a very nonlinear dependence. It is not known whether this is typical, or special to that transition.

With a simulation capability based on accurate free energies [2, 3] and the model given by Eq. (2), it has been possible to contribute to the design an interpretation of a number of experiments. Figure 1 shows the results of a simulation of an isentropic compression experiment (ICE) on Zr carried out at the Sandia Z-machine.

Because of the complicated interaction of waves with material interfaces in these experiments, their interpretation is not obvious, and simulations play an important role. The large "notch" near the peak of the wave is clearly associated with a second phase transition from ω to bcc, and is well predicted by the simulation, which has no parameters adjusted to this experiment. Figure 2 shows a picture in spacetime of the complex wave interactions when a shock wave induces a phase transition in Sn.

The models used here for the rates R_{ij} are simple and phenomenological. The resulting simulations are useful for interpreting shock wave experiments, but are not predictive regarding effects of temperature or impurities on transformation rates. The combination of more microscopic theories and simulations with experiments such as sample recovery will be needed to develop more predictive models. The framework described here will allow the resulting improved models to be compared with macroscopic experiments.

For more information contact Carl Greeff at greeff@lanl.gov.

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Funding Acknowledgements
NNSA's Advanced Simulation and Computing (ASC), Physics and Engineering Models.

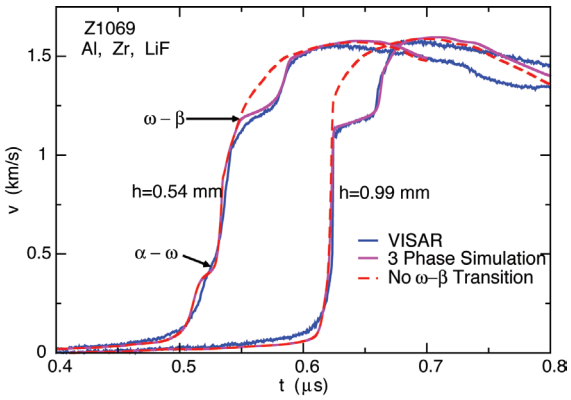

Fig. 1.
Simulations of isentropic compression experiment on Zr (P.A. Rigg, DX-2). The sample was loaded with a smooth magnetic compression wave. Blue curves are experimental VISAR traces. Magenta curve is simulation with 3-phase EOS. Dashed red curve is simulation with second phase transition turned off.

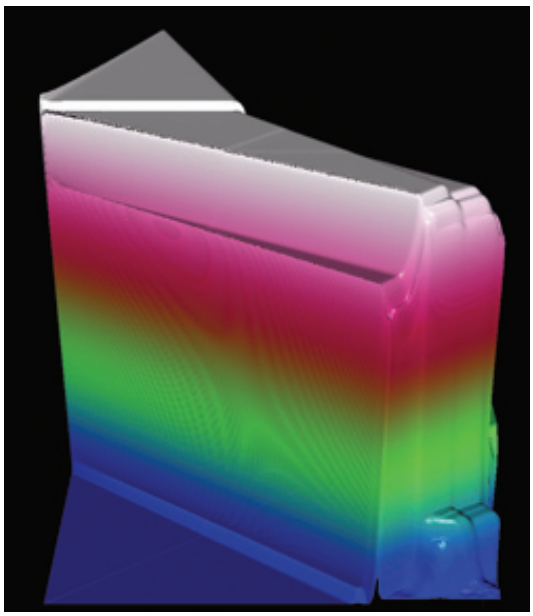

Fig. 2.
Pressure surface in spacetime for Sn sample subject to impact loading. Time advances to the right and space coordinate is out of the page. Viewpoint is from Sn free surface with impactor in the back. The "shelf" in the pink part of the wave is due to the β-bct phase transition.